

## **Declaration of André Sijpkes**

1. I, the undersigned, André Harmen Sijpkes, a citizen of The Netherlands, am a Laboratorium Manager at Avantium. I received my PhD in Physical Chemistry in 1990 at the Free University in Amsterdam. Since 1993 I worked first at Shell in catalyst development and since 2000 at Avantium as a catalyst preparation expert. It is my understanding that United States Patent Application No. 10/583,010 ("Patent Application") has been rejected as being obvious over Satoru et al (EP 895809) in view of Shaw et al (US 4,280,929), as set forth in the non-final Office Action mailed January 21, 2010.
2. Our patent application 10/583,010 teaches a specific preparation of a catalyst, which results in a catalyst with a specific structure and excellent results as catalyst in alkane or alkene (amm)oxydation.
3. The examiner has stated in the non-final Office Action mailed January 21, 2010, that Satoru describes a multicomponent catalyst that can be used for the production of (meth)acrylic acid and (meth)acrylonitrile in high yield. Further, the examiner states that Shaw teaches that it has been discovered that the use of fumed silica in catalyst preparation followed by an addition of silica results in a catalyst having better physical strength for operation and greater activity and selectivity than the prior art supported catalysts. Shaw identified prior art carriers to be silica sol. According to the examiner it would have been obvious to one of ordinary skill in the art at the time of the invention to utilize the fumed silica of Shaw with the catalyst of Satoru.
4. In 2002 and 2003 Avantium carried out a discovery project covering a large number of variables in the catalyst preparation of multimetal oxides similar to the one described in the Patent Application. Based on this research Avantium developed the preparation method for a multioxide catalyst, and the catalyst thus obtainable, as described in the Patent Application.
5. In a further research effort two catalysts were prepared again and characterized extensively by means of XRD, TEM/EDX, and pore structure analysis (see attached

Experimental Report). The catalysts were tested in a similar test under conditions described in the Patent Application. The results show that the catalyst prepared with fumed silica, i.e., a ceramic silica in the form of a substantially dry powder, (Aerosil 300) outperformed the one prepared with a silica sol (Ludox). Also the catalysts were shown to have significantly different properties with regard to surface characteristics and metal distribution.

6. I conducted the catalyst preparation by spray drying two slurries/solutions prepared from the various solutions that make up the components of the catalyst, with either fumed silica (Aerosil 300) or silica sol (Ludox) as a support, as described in the Patent Application. Following the spray drying the catalyst precursors were further treated at elevated temperatures, first under an air flow and second under an argon flow to obtain two final catalysts, denoted by Comparative Example 1A and 1B. In all unit operations of preparation the conditions and compositions of the solutions were exactly the same for both catalysts, the only difference being the nature of the silica precursor. The catalysts were characterized by XRD, TEM/EDX, and pore structure analysis, the results of which are described in the attached report. The two catalysts were tested in one of Avantium's test units alongside each other under the exact same conditions of flow, pressure and temperature, as described in the Patent Application and the attached experimental report.

7. The results show that the two catalysts differ in a number of significant ways regarding their physical properties (surface metal distribution, pore structure), and the test data show that the catalyst prepared with the fumed silica has a significant higher overall yield than the catalyst prepared with the silica sol. This is contrary to the disclosure in Shaw where a catalyst prepared using silica sol as sole source for the carrier gave a higher yield of acrylic acid than the catalyst wherein fumed silica was applied as part of the silica source.

The undersigned declares that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section

1001 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of the above captioned application or any patent issuing thereon

24 MARCH 2010

Date



André H. Sijpkes

Attachment: Experimental report

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# Experimental Report

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Andre Sijpkes

Avantium

September/October 2009

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Additional experiments have been performed to demonstrate the effect of the AVT catalyst over the Ludox catalyst in the oxidation of propane to acrylic acid.

- 5 The experimental set-up was as described in WO2005/058498 with reference to the examples therein.  
The results of the experiments (comparative 1A and 1B) are described herein below (table 1) side by side with the experiments that were earlier performed for the patent application.

10 The catalysts have been characterised as described herein below.  
The catalysts have been tested in the oxidation of propane to acrylic acid at a temperature of 350-370-390-410 degrees Celsius. The results are presented in annex 1

15 Conclusions:

- The physical properties of the Ludox based catalyst differ significantly from those of the Aerosil based catalyst.  
Elemental analysis in TEM measurements shows that the Aerosil  
20 type of catalyst has an enrichment of metals on the surface of the particles compared to the slurry composition used during spray-drying. The calcined Ludox based catalyst has less metals on the surface than applied in the slurry.
- At a Space Velocity (SV) of 1200 h<sup>-1</sup> the AVT catalyst (yellow or light grey in the figures of Annex 1) is consistently better than the Ludox based catalyst (blue or dark grey), increasing Space Time Yield (STY = mass of product per volume of reactor and time in kg m<sup>-3</sup> s<sup>-1</sup>) with increasing temperature from 350 and 410°C. There is no such trend for the Ludox  
25 based catalyst, as can be seen in the STY plot in Annex 1.  
The shift in STY at 150 hours is caused by an increase in propane concentration (above 3.3% described in the patent). At this point the feed concentration of propane is doubled in order to try and increase productivity. This different feed  
30 is indicated by round markers, the original feed (3.3% propane) is indicated by square markers. After a few data points with increased propane concentration the feed is brought back to the original composition to test whether any  
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damage has been done to the catalysts (which is not the case) .

Table 1. Catalyst test results ( $\text{Mo}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$  catalyst compositions). Observed at 410°C in the oxidation of propane to acrylic acid.

Catalyst	Drying method	Support	%wt metals	Conv. C <sub>3</sub>	Selectivity AA	Yield AA	Pore structure
			(%)	(%)	(%)	(%)	(mL/g) (g/mL)
Ex. 1	SD	Aerosil 300	33.9	40	75	30	0.28 50
Ex. 2	RV	Aerosil 300	33.9	38	77	29	0.37 45
Comp. Ex. 1	RV	Ludox	33.9	n.d.	n.d.	n.d.	1.26 202 0.6
Add. Ex. 1A	SD	<b>Aerosil 300</b>	<b>33.9</b>	<b>49</b>	<b>83</b>	<b>41</b>	<b>0.28 38 1.8</b>
Add. Ex. 1B	SD	Ludox	33.9	63	19	12	0.12 23 2.5
Comp. Ex. 2	SD	None	67.8	30	64	19	0.02 5.9 4.5
Comp. Ex. 3	RV	none	67.8	55	45	25	0.02 6.3 4.5

SD = spraydrying; RV = rota-evaporation, C<sub>3</sub> Conv. = conversion of propane (percentage)

AA Selectivity = selectivity of propane conversion to acrylic acid (in percent)

AA Yield = the yield of acrylic acid (in percent)

PV = pore volume, SA = surface area

APD = Apparent Particle Density, defined as  $(1/\text{SKD} + \text{PV})^{-1}$ , where SKD is the Skeletal Density. The SKD is the sum of the component densities ( $\sum_i X_i d_i$ , with  $X_i$  the weight fraction and  $d_i$  the density of the i-th component).

## Summary of physical characterization experiments

### 1. Pore structure: see Table 2.

The Ludox catalyst has a significantly lower pore volume and lower surface area than the Aerosil catalyst.

Table 2		PV	SA	APD
Catalyst		(mL/g)	(m <sup>2</sup> /g)	(g/mL)
Comp. Ex. 1A	0.28	38	1.8	
Comp. Ex. 1B	0.12	23	2.5	

### 2. XRD analysis:

There is no significant difference between the Aerosil and the Ludox based catalysts.

### 3. TEM:

The surface concentrations of the metals in the Ludox and Aerosil based catalysts change in different ways during the drying and calcination, see Table 3. In the Aerosil based catalyst there is a pronounced surface enrichment in Mo, V, Nb, and Te, first after drying and further upon calcination, whereas in the Ludox based catalyst there is a decrease in Mo, a slight increase in V and Nb, while Te does not change upon calcination.

Table 3. Surface metal concentrations in Ludox and Aerosil based catalysts (as measured by TEM, average values as measured on 3 particles per samples and 8 spots per particle).

Metal	Theoretical (Bulk) composition	Ludox Spraydried (dried, not calcined)	Ludox calcined	Aerosil Spraydried (dried, not calcined)	Aerosil calcined
Si	23.4	19.2	21.1	20.0	11.7
Mo	21.4	17.8	18.0	22.5	24.5
V	3.4	4.3	4.3	3.1	5.8
Te	6.6	9.2	6.3	4.3	9.0
Nb	2.5	4.5	3.6	3.1	3.5

Note: the remainder of the composition is oxygen. The composition is in % relative to the total mass.

### 4. Particle size distribution:

The Aerosil based catalyst shows a broad distribution around 5 micron, whereas the Ludox shows a sharp peak around 3 micron.

Annex 1

